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(54) Title: **OPEN CELL FOAMED ARTICLES**

(57) Abstract: An open cell foamed polyolefin article is obtained by providing a polymeric composition comprising a functionalized polyolefin comprising functional moieties reactive to ammonia, and a chemical foaming agent capable of producing ammonia, and activating the chemical foaming agent to generate a gaseous blowing agent and ammonia, whereby the blowing agent forms an open cell foam article and the ammonia chemically crosslinks the polyolefin at the ammonia-reactive sites.

## OPEN CELL FOAMED ARTICLES

5

### Background of the Invention

Flexible polyurethane foam is used in many industrial areas, for example as automotive, furniture and packaging materials. However, polyurethane foam has the disadvantages of poor weatherability and water  
10 resistance. The most popular open-cell foams derived from polyurethane degrade easily when exposed to ultraviolet rays and ozone.

Polyolefin foams are considerably more durable than polyurethane and are used in large quantities as heat insulating materials, packaging materials, and cushioning materials. They are typically closed-cell, and  
15 therefore are not suitable for applications where water absorptivity and breathability are required. Currently available breathable, open-cell polyolefin foams are coarse in cell size, poor in hand, and have limited applicability. A crosslinked foam of a polyolefin obtained according to a usual method has an open cell percentage of less than 20%, yielding a  
20 foam product that is not retentive and inflexible.

Some open-cell foam articles are available. For example, US patent 5,348,795 describes a polyolefin open cell foam prepared by direct foaming. The resultant foam is not crosslinked or lightly crosslinked, so it has very little thermal stability and resilience. US Patent Nos. 3,950,278  
25 and 4,424,181 also describe lightly crosslinked polyolefin open cell foam articles. US Patent No. 4,501,711 shows polyolefin open cell foam with chemical crosslinking using very low molecular weight ethylene-vinyl

acetate copolymer (EVA). These articles have better thermal stability than non-crosslinked polyolefin open cell foams, but are still not good enough to satisfy general demand.

5 In other processes, a crosslinked foam has first been prepared and the resulting product has then been subjected to a secondary processing to destroy the closed cells for conversion to open cells by heat expansion. This process gives rise to a foam that lacks resiliency and causes "bottom-out". In addition, uniform cell opening is difficult to achieve and the resulting cells are coarse in size. In an alternative process, an open cell  
10 foam is prepared by pressing closed cells causing the cells to rupture. The process described in US Patent No. 5,859,076 to Kozma et. al creates new open cell foam by a crushing process; however, the process also damages the overall foam properties.

Known methods produce open cell foams that are flexible, but  
15 without thermal or dimensional stability. There remains a need for an open cell polyolefin foam that has both flexibility and thermally stability.

Known methods produce open cell foams of non-uniform or coarse cell size. There remains a need for an open cell polyolefin foam having a high percentage of open cells that are of uniform size and consistency.

20 It is an object of the present invention to produce an open cell polyolefin foam of high crosslink density.

It is a further object of this invention to provide a method for preparing an open cell polyolefin foam that is flexible, resilient and possesses good thermal stability.

25 It is a further object of the invention to provide an open cell polymer foam of low density having a high percentage of open cells and a consistent and uniform cell size.

These and other objects are achieved by the invention, which follows.

#### Summary of the Invention

5       According to the invention, an open cell polyolefin foam of excellent thermal stability, flexibility and resilience is obtained by coordinating the progression of the foaming and crosslinking reactions so that a high level of crosslinking is achieved only after the open cell structure of the polymer is formed.

10       In one aspect of the invention, a process for producing open cell, cross linked polyolefin foam article includes providing a polymer composition including a functionalized polyolefin having reactive moieties that are reactive to ammonia, and a foaming agent wherein a majority of the foaming agent is a chemical foaming agent capable of  
15       producing ammonia. The chemical foaming agent is activated to generate a gaseous blowing agent and ammonia, whereby the blowing agent forms an open cell foam article and the ammonia chemically crosslinks the polyolefin at the ammonia-reactive sites. Because the primary crosslinking agent, ammonia, is generated as a by-product of the foaming  
20       agent decomposition, crosslinking does not occur until foaming is substantially complete.

      In another aspect of the invention, a method for a producing an open-celled, cross linked polycarbonate foam article includes providing a polymer composition comprising a polycarbonate having a functional  
25       moiety reactive to ammonia and a foaming agent wherein the foaming agent is a chemical foaming agent capable of producing ammonia, activating the chemical foaming agent to generate a gaseous blowing agent

and ammonia, whereby the blowing agent forms an open cell foam article and the ammonia chemically crosslinks the polycarbonate at the ammonia-reactive sites.

The term "closed cells" used herein means cells in which bubbles  
5 are surrounded by resin membranes in the foam and are not interconnected or open to adjacent cells of the foam. The term "open cells" means cells made up of resin membranes of the foam that are interconnected and open to adjacent cells of the foam.

A "foaming agent" is a compound used to introduce cells or pores  
10 into a polymer resin. By "chemical foaming agent" is meant a compound, or mixture of compounds, that decomposes or reacts at elevated temperatures to generate one or more gases, which form pores or cells in a polymer resin. The chemical foaming agent may generate gases by decomposition or when heated to form gaseous products. A "physical  
15 foaming agent" is a gas or volatile compound that is in a vapor state at use temperatures to form pores or cells in a polymer resin.

By "functionalized polyolefin" is meant a polyolefin containing functional groups along the polymer backbone or pendent to the polymer backbone. A functionalized polyolefin is "reactive to ammonia" if it  
20 contains a chemical moiety along the polymer backbone or pendent to the polymer backbone that is capable of undergoing chemical reaction with ammonia. Exemplary reactive moieties include carbonyl, epoxide, anhydride and organic acid groups.

A "crosslinkable" polymer is one that contains a chemical moiety  
25 along the polymer backbone or pendent to the polymer backbone that is capable of undergoing chemical reaction with a crosslinking agent to form a crosslink, or which is capable of being activated so that the polymer

backbone undergoes crosslink, e.g., by activation with peroxides to induce free radical-initiated crosslinking. At least some of the crosslinkable chemical moieties are reactive to ammonia.

By "resin" is meant a natural or synthetic polymer.

5 "Gel fraction" is used to describe the degree of crosslinking and may be determined by extraction with a solvent such as xylene.

#### Brief Description of the Drawing

The invention is described with reference to the Drawing, which is  
10 presented for the purpose of illustration only and is in no way limiting of the invention, and in which:

Figure 1 is a plot of increasing pore content vs. gel fraction and illustrates the composition of materials in the prior art and the current invention; and

15 Figure 2 is an exemplary reaction scheme for the crosslinking of a polyolefin at a CO-site.

#### Detailed Description of the Invention

The materials of the present invention are described with reference to  
20 Figure 1. In order to obtain a foam of high thermal stability and high resilience, it is desirable to form a foamed article of high crosslink density. Crosslinking of polyolefin foams is known. For example, peroxide crosslinking or silane-water crosslinking is commonly used to obtain a crosslinked polyolefin foam. See, U.S. Patent No. 4,900,490 and  
25 5,883,145, respectively. However, in these conventional processes, the reaction that generates the blowing agent competes with the reaction that chemically crosslinks the polymer so that the two processes do not take place in a complementary fashion. If the crosslinking reaction takes place

too quickly, a highly crosslinked polymer is formed before the material is fully foamed. The resultant foam is undesirably dense, producing a polyolefin article in the relative open cell-gel fraction regime delineated by region 10. Typically, an open cell structure is not formed because the crosslinked polymer is too tough to rupture the cell walls. Alternatively, if the crosslinking reaction occurs too slowly, foaming is complete before the crosslinking reaction has progressed to any significant degree, and the foam may form thin walls and/or collapse in on itself to produce a foam of irregular or coarse cells, as is illustrated by a materials regime delineated by region 20. The prior art has described mechanical rupture of closed cells for the purpose of enhancing open cell content of the foam, which is shown as region 30. Mechanical processing typically damages such foams.

According to the invention, an open cell polyolefin foam of excellent thermal stability, flexibility and resilience is obtained by coordinating the progression of the foaming and crosslinking reactions so that a high level of crosslinking is achieved only after the open cell structure is formed, thereby providing a foamed article in the regime delineated by region 40. As used herein, open cell foam means a foam possessing an interconnection or opening between adjacent cells. There can be greater than about 40% open cells, preferably greater than 60%, more preferably greater than 80%. To provide adequate thermal stability, the gel level should be greater than 50%, preferable 60%, and more preferably greater than 70%. In particular, the foams of the invention exhibit dimensional change of less than 10% at 70 °C and a compression set of less than 12%.

In one aspect of the invention, a process for producing an open cell crosslinked polyolefin foam article includes providing a polymer

composition including a functionalized polyolefin having functional moieties that are reactive to ammonia and a chemical foaming agent capable of producing ammonia. The chemical foaming agent is activated to generate a gaseous blowing agent and ammonia ( $\text{NH}_3$ ), whereby the blowing agent forms an open cell foam article and the ammonia chemically crosslinks the polyolefin at the ammonia-reactive sites. This reaction helps to enhance the thermal stability of the open cell foam by crosslinking the resin after foaming has taken place or after a significant degree of foaming is complete.

The process employs a polymer resin that can react with  $\text{NH}_3$ , for example, a polyolefin functionalized with carbonyl, organic acid, anhydride or epoxide groups. Polyolefins include polymers of ethylene and propylene, including high density polyolefin and low density polyolefin, and mixtures thereof. It also includes conventional polyethylene copolymer derivatives, such as vinyl ester, alkyl acrylate and alkyl methacrylate and  $\alpha$ -olefin copolymers of polyethylene. It also may include polymer blends. For example, the polyolefin may be blended with polymers such as polyethylene (PE), polypropylene (PP) and ethylene vinyl acetate (EVA). Suitable blends are those, which provide a polymer resin having a melt index in the range of about 0.3 to 50, and preferably about 0.3 to 10. PE, PP, and EVA have melt indices in the range of 0.3 to 50.

Functionalized polyolefins may be prepared using well-known methods. For example, unsaturated monomers having the desired ammonia-reactive functional group may be used in the preparation of the polyolefin. Reactive unsaturated monomers that may be used to obtain suitable functionalized polyolefins include any monomer having a group



that can react with  $\text{NH}_3$ , for example, carbon monoxide, maleic anhydride, epoxide, glycidyl methacrylate, acrylic or methacrylic acid or and the like.

Commercially available polyolefin resins may be used in the practice of the invention. For example, suitable carbonyl-functionalized polyolefins include Elvaloy® 741, 742, 4924, HP441 (Dupont) and the like, which is a polyolefin resin containing a carbonyl group (derived from carbon monoxide). Exemplary acid-functionalized polyolefins include Fussabond® (Dupont) and Polybond® (Witco), which are polyolefin resins containing maleic anhydride and/or acrylic groups. Suitable epoxide-functionalized polyolefins include Elvaloy® PTW (Dupont). These commercially available resins are commonly used as asphalt modifiers or polymer plasticizers.

The level of ammonia reactive functional group may vary. In preferred embodiments, at least 1 wt%, and preferably at least 3 wt% of the monomer source for the ammonia-reactive functional moiety is used. The olefin content of the polymer resin should be at least 60 wt%, and preferably the monomer source for the ammonia-reactive functional moiety is no more than 20 wt% of the polymer resin. For example, Elvaloy® 741, 742 and 4942 has 10-12% content of functional group by weight and around 70% polyolefin content. Polybond® includes 1-6% acrylic acid and maleic anhydride and 94-99% polyolefin. The functional group content provides an upper limit to the degree of crosslinking obtainable by reaction with ammonia.

The foaming agent includes a compound or mixture of compounds, which generates an inert gas such as nitrogen by thermal decomposition, and which also produces ammonia as a by-product when it decomposes. Ammonia is traditionally considered an undesired by-product of the foaming reaction because it is corrosive and represents an environmental

hazard requiring additional safety precautions when handling. Most compounds considered suitable for use as foaming agents produce low levels of ammonia as a by-product, typically in the range of 1-5% wt% of gaseous product. The actual amount will vary depending upon the  
5 foaming agent.

An exemplary reaction between an ammonia-reactive functional moiety and ammonia is shown in Figure 2. Compound 100 represents a polyolefin containing a carbonyl functional group and may be, for example, an Elvaloy polymer resin. The carbonyl group reacts with  
10 ammonia, most likely through ammonia nucleophilic attack on the electropositive carbonyl carbon, although the invention is not limited to any particular mode of action or reaction. The reaction product may be compound 110 having a crosslink 120 between adjacent polymer strands. The crosslink includes a nitrogen atom, whose source is the ammonia  
15 reactant.

Conventional chemical foaming agents may be used in the practice of the invention, provided that they produce ammonia. Suitable chemical foaming agents include azo compounds such as azodicarbonamide, p-toluenesulfonyl semicarbazide, 5-phenyltetrazole, nitroso compounds,  
20 such as N,N'-dinitrosopentamethylene-tetramine, and aromatic hydrazides, such as p,p'-oxybenzenesulfonyl hydrazide may generally be used as the foaming agent. These chemical foaming agents may be used singly or in combination.

It is also within the scope of the invention to include a minor  
25 amount of physical blowing agents such as volatile organics or other similar vaporous compounds. Such blowing agents may be added at low levels, e.g., less than 50 wt% of total foaming/blowing agent, and preferably in the range of 0-15 wt%, and include aliphatic hydrocarbons

having 1-9 carbon atoms, halogenated hydrocarbons of 1-4 carbon atoms, and aliphatic alcohols of 1-3 carbon atoms. Other suitable blowing agents include carbon dioxide, nitrogen, argon, water, air, nitrogen or helium. Addition of physical foaming agents may be desired to produce a very low  
5 density foam.

In general, the foaming agent will have a decomposition temperature (with resultant release of gaseous materials) in the range of about 180-250°C, and preferably in the range of about 180-230 °C, and for example about 220 °C. In preferred embodiments, the temperature of  
10 decomposition is selected to produce the desired level of ammonia by-product. At higher temperatures, more ammonia is produced. For example, when using azodicarbonamide, ammonia is 5% of the gaseous product at 250°, but only 1% of the gaseous product at 180-190°C. In currently preferred embodiments, the decomposition is carried out at  
15 220°C. Additives may be included in the polymer composition to alter the temperature of decomposition. In order to lower the decomposition temperature of the foaming agent, a foaming adjuvant, such as stearic acid or zinc stearate, may be used; for example, in a proportion of 5 or less parts by weight per 100 parts by weight of the total resin  
20 components. The amount of the foaming agent may be varied depending upon the desired expansion ratio, though the foaming agent is preferably used in amount of 1 to 50 parts by weight per 100 parts by weight of the total resin component, and preferably about 5-25 parts per 100 parts total resin component.

25 Since crosslinking is a result of the ammonia-level generated upon decomposition of the foaming agent, the foaming agent is a factor in determining the degree of crosslinking. The degree of crosslinking may be controlled by both the amount of foaming agent and foaming time. In a

resin system employing Elvaloy 4924 as the ammonia-reactive polyolefin and azodicarbonamide as the foaming agent, an 80% gel fraction was obtained with 15 phr (parts per hundred parts resin), while a 65% gel fraction was obtained with 7.5 phr.

5 Additional crosslinking agents may be used, but are not required. In particular, it may be desirable to include a secondary crosslinking agent, which is not activated under the conditions of foaming and crosslinking with ammonia. Once the foaming and preliminary crosslinking using ammonia is completed or substantially complete and the foam open cell  
10 structure is established, the secondary crosslink agent may be used to increase the crosslink density and, thereby, the thermal stability of the foam.

In one embodiment, the secondary crosslinking agent may be one that reacts more slowly than ammonia, so that the ammonia reaction is  
15 substantially complete before the second crosslinking agent can react. In other embodiments, the secondary crosslinking agent may be one that does not react under conditions established for the foaming agent decomposition and ammonia reaction. Once these reactions are complete, conditions may be altered to initiate the secondary crosslinking reaction.  
20 For example, a secondary crosslinking agent may be selected which does not react at the temperature selected for foaming agent decomposition. Thereafter, the temperature may be raised to initiate the second crosslinking reaction.

Suitable crosslinking agents include an organic peroxide that can  
25 thermally be decomposed, preferably at a temperature other than that used to initiate foaming. The organic peroxide used in this process has a 1 hour half-life temperature of between 110°C and 200°C. Examples of suitable

secondary crosslinking agents are 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane-3, di-tertiary-butyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne, tert-butyl cumyl peroxide, di-(2-tert-butylperoxyisopropyl)benzene, dicumyl peroxide, butyl 4,4-di-(tert-butylperoxy)valerate, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, and tert-butyl peroxybenzoate. The proportion of the crosslinking agent is preferably 0.1 to 4 parts by weight per 100 parts by weight of the total resin components.

Regardless of the method of crosslinking used, acceptable foam articles are typically obtained in certain ranges of crosslinking density or level. Too much crosslinking can render the foam inelastic and lacking resiliency. Too little crosslinking can be detrimental to physical properties such as compression or thermal stability. It is desirable to select crosslinking levels that provide the foam with the desired performance properties. Suitable crosslink levels may be determined by the level of functional moiety incorporated into the functional polyolefin. In preferred embodiments, at least 3 wt% and preferably no more than 20 wt% ammonia-reactive functional moiety is used. The degree of crosslinking is also controlled by the level of crosslinking agent used, including both the ammonia and secondary crosslinking agent.

Crosslinking level is defined by the gel content of the composition, and may be in the range of 25% to 98%. In preferred embodiments, gel fraction is preferably in the range of greater than 50%, preferable 60%, and more preferably greater than 70%. When a higher gel fraction level is desired than is obtainable from ammonia crosslinking alone, secondary crosslinking agents, such as peroxide, may be used to increase the gel fraction. Gel content may be determined, for example, by extraction with a solvent such as xylene. In particular, gel fraction is defined as

$100 \cdot W_g / W_s$ , where  $W_g$  is the initial weight of the sample and  $W_s$  is the weight of the sample after heating in xylene for 24 h at 120 °C.

In other embodiments, coloring agents, surfactant, foaming kicker, anti-oxidant, UV stabilizer, anti-bacterial agents, flame retardant, lubricant, adhesion promoter, process aids, colorants, monomer and/or other resins and/or fillers may appropriately be blended with the above composition to meet application criteria.

Any surfactant suitable for polyolefin, for example, polyether modified silicone fluid, methylstyryl modified silicone fluids and alkyl modified and the like may be used. A surfactant may be used to stabilize bubbled formed during the foaming operation. It will be immediately apparent to one of ordinary skill in the art which of the many available surfactants are appropriate to improve foam stability.

The fact that the foaming agent composition of this invention may take any form means that open-cell foam can be produced from pellets, powder, film, and sheet. The foams can be produced both in a continuous in-line process or batch process. In the technology of this invention it is desirable that the polymer composition is mixed using an extruder or kneader and is prepared below the temperature at which the foaming agent decomposes. The compounded composition is formed into the desired shape and is then heated to the foaming agent decomposition temperature to make open cell foam.

By way of example, methods of combining the components of the foamable mixture include melt-blending or liquid mixing. Any or all of the ingredients may be pulverized or comminuted by conventional methods. Melt-blending can be accomplished in a batch or continuous process, using for example, an internal mixture such as a Banbury mixer, a single or twin screw extruder, or roll mills. It is preferred that mixing be

carried out under temperature control, in particular to avoid premature decomposition of the foaming agent. Components can be added together or sequentially. Once mixed, the blend can be formed into a desired shape, for example, sheets by passing the blend through a two roll mill.

- 5 The sheets can be cut into any desired shape and heated to initiate the foaming and crosslinking process. Alternatively, the blend may be shaped in a continuous extrusion process, or by compression molding. The time and temperature of the foaming process may be modified to obtain a foam of optimized properties.

- 10 In some embodiments of the invention, the open-cell content of the foam or its permeability to gases and fluids may be enhanced by mechanical means. For example, the foam may be crushed or mechanically perforated. The inventive foamed articles form open cells more readily when crushed than conventional closed-cell polyolefin
- 15 foams. While not bound by any particular mode of operation, it is hypothesized that formation of additional open cells occurs more readily once cell walls have been perforated initially in the foaming step. The foamed article may be crushed by passage through feed rollers with decreasing nip thicknesses. The gap between rollers is arranged so as to
- 20 decrease as the foam passes between successive rollers, crushing the foam and causing remaining closed cells to rupture, and thereby increasing the open cell content of the foam. Due to the high resiliency of the inventive foam articles, they recover readily from the crushing operation and quickly regain their original shape and thickness. In other embodiments, the
- 25 rollers may include pins on their surfaces that penetrate the foam and further increase the open cell content of the foam. The pins may be used

on one or both rollers, and may have a variety of shapes. The foam may be crushed at temperatures at which the article is thermally stable, for example in the range of about 50 °C to 100 °C.

The open cell foam articles of the invention have good  
5 weatherability, as is typical for polyolefin compositions. They also are permeable fluids and gases. The foams may be used in a variety of applications, such as packaging and insulation.

In another aspect of the invention, open cell, crosslinked foams containing polycarbonate may be prepared using the method of the  
10 invention. Thus a polymer composition is provided, which includes a polycarbonate, and a foaming agent wherein a majority of the foaming agent is a chemical foaming agent capable of producing ammonia. The chemical foaming agent is activated to generate a gaseous blowing agent and ammonia, whereby the blowing agent forms an open cell foam article  
15 and the ammonia chemically crosslinks the polycarbonate at the ammonia-reactive sites. Common polycarbonates include polycarbonates of bisphenol. Because the polymer resin itself inherently includes the ammonia-reactive sites, i.e., the carbonate group,  $O-(C=O)-O$ , of the polymer, no additional modifications of the polymer resin is required.  
20 Because the level of ammonia-reactive sites can be high, it may be desirable to include co-monomers that reduce the carbonate content of the polymer resin. Other additives and formation considerations discussed herein above for polyolefin foams are expected to be relevant to the formation of a polycarbonate foam.

25 The invention is described in the examples that follow, which are provided for the purpose of illustration only and are not intended to be limiting of the invention.



Example 1-6

Functionalized polyethylene (Elvaloy 4924)<sup>1</sup>, polyethylene  
 copolymer (Elvax 265), surfactant (silicone fluid), foaming adjuvant  
 (stearic acid), foaming agent (azodicarbonamide), foaming catalyst (zinc  
 5 oxide), and antioxidant (Mark 328, Uniroyal Comany) were combined in  
 the amounts listed in Table 1.

Table 1.

Ex.	Elvaloy 4924 <sup>1</sup>	Elvax 265 <sup>2</sup>	Surfactant <sup>3</sup>	Stearic Acid <sup>4</sup>	FA <sup>4</sup>	ZnO	Mark 328
1	100	0	1	0	25	0	0.5
2	100	0	1	2	25	0	0.5
3	100	0	1	0	25	0.2	0.5
4	100	0	1	2	25	0	0.5
5	100	0	1	0	25	0.2	0.5
6	75	25	1	0	25	0.2	0.5

10 <sup>1</sup> Elvaloy 4924 is supplied by Dupont, terpolymer of ethylene, vinyl acetate  
 and carbon monoxide MI=9.

<sup>2</sup> Elvax 265 is supplied by Dupont, copolymer of ethylene and vinyl acetate  
 (VA=28%), Mi=3.0.

15 <sup>3</sup> Surfactant is KF412, an alkyl-modified silicone fluid supplied by Shinetsu  
 Silicones of America.

<sup>4</sup> FA is azodicarbonamide, (Celogen 150 supplied by Uniroyal Company).

In the above examples 1 through 6, these ingredients were combined  
 and mixed on a 3 inch roll mill. The roll temperatures were set at 250°F  
 20 and 190°F, resulting in the blending and melting of the resin composition.  
 The melted resin was pressed at 10MPa and cooled from 250°C to room  
 temperature to obtain 6" by 6" sheets of 1mm thickness. The sheets were

irradiated using a 1.2 Mrad electron beam to polymerize. Each sheet was then foamed horizontally on talc particles in a mechanical convection oven at 220°C.

The foam and mechanical properties of each sample evaluated and  
5 are listed in Table 2.

Table 2.

Ex.	Density (kg/m <sup>3</sup> )	Open Cell Ratio	Gel Fraction	Dimensional Change at 70°C <sup>2</sup>	Compression Set @ 50% <sup>2</sup>
1	40	95%	62%	7%	10%
2	50	90%	58%	8%	11%
3	50	80%	55%	9%	12%
4	60	80%	55%	8%	12%
5	50	80%	55%	8%	12%
6	50	80%	53%	8%	12%

<sup>1</sup> Open Cell Ratio is determined according to D2856-94 by ultrapycnometer  
10 1000 supplied by Quantachrome.

<sup>2</sup> Dimensional Change and Compression Set are determined according to ASTM  
D3575-93

Compression was determined according to ASTM D3575-93 as  
15 follows. The test specimens were cut into 50 mm by 50 mm squares and  
stacked to a thickness of about 25 mm to provide an initial sample  
thickness (t(0)). The samples were placed in a compressive device and  
compressively deflected to 50% of their original thickness for 22 hours.  
Final thickness (t(f)) was measured after allowing for a 24 hour recovery.  
20 Compression set is defined as  $100 \cdot (t(0) - t(f)) / T(0)$ .

Dimensional change was also determined under ASTM D3575.

The test specimens were cut into 250 mm by 250 mm squares and the length ( $L(0)$ ) was determined. The samples were then placed in an oven temperature controlled at 70 °C for 24 h. The sample was then removed  
5 and cooled at room temperature for 2 h before measuring the length ( $L(f)$ ). The %dimensional change is defined as  $100 \cdot (L(f) - L(0)) / L(0)$ .

These results show that foamed polyethylene articles prepared using ammonia-reactive functionalized polyethylene possess high levels of open cells (80-95%) and high levels of crosslinking (53-62% gel fraction).  
10 Furthermore, the exception compression set values (10-12%) make these materials suitable for use as seals and cushioning. Due to their demonstrated thermal stability (dimensional changes of 7-9%), they are also suitable for use in high temperature environments.

15 What is claimed is:

1. A method for producing an open-cell, crosslinked polyolefin foam article, comprising:
  - (a) providing a polymer composition comprising:
    - (i) a functionalized polyolefin comprising a functional moiety reactive to ammonia, and
    - (ii) a foaming agent wherein a majority of the foaming agent is a chemical foaming agent capable of producing ammonia; and
  - (b) activating the chemical foaming agent to generate a gaseous blowing agent and ammonia, whereby the blowing agent forms an open cell foam article and the ammonia chemically crosslinks the polyolefin at the ammonia-reactive sites.
2. The method of claim 1, wherein the foaming agent comprised a chemical foaming agent and a physical foaming agent, the physical foaming agent present in an amount of less than 15 wt% total foaming agent.
3. The method of claim 1, wherein the polymer composition is formed into a desired shape prior to foaming.
4. The method of claim 3, wherein the polymer composition is formed into a shape selected from the group consisting of pellets, sheets, powders and films.
5. The method of claim 1, wherein the chemical foaming agent is selected from the group consisting of azodicarbonamide, p-toluenesulfonyl semicarbazide, 5-phenyltetrazole or combinations thereof.

6. The method of claim 1, wherein the chemical foaming agent is in the amount in the range of about 1-50 parts by weight per 100 parts by weight polyolefin.

5        7. The method of claim 1, wherein the chemical foaming agent is in the amount in the range of about 5-25 parts by weight per 100 parts by weight polyolefin.

8. The method of claim 1, wherein the polymer composition  
10 further comprises a crosslinking agent.

9. The method of claim 8, wherein the polymer composition is heated to a first temperature to activate the foaming agent, and thereafter the polymer composition is heated to a second  
15 temperature to activate the crosslinking agent.

10. The method of claim 8, wherein the crosslinking agent is a peroxide.

20        11. The method of claim 1, wherein the functional moiety is selected from the group consisting of carbonyl, epoxides, anhydrides and organic acid groups.

12. The method of claim 1, wherein the ammonia-reactive  
25 functional moiety comprises at least 3 wt% of the functionalized polyolefin.

13. The method of claim 1, wherein the ammonia-reactive functional moiety comprises at least 5 wt% of the functionalized polyolefin.

5        14. The method of claim 1, wherein the ammonia-reactive functional moiety comprises 1-20 wt% of the functionalized polyolefin.

15        15. The method of claim 1, wherein the polymer composition has a melt index in the range of 0.3 to 10.

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16. The method of claim 1, wherein the polymer composition further comprises a surfactant.

15        17. The method of claim 1, wherein the polymer composition further comprises a second polyolefin.

18. The method of claim 17, wherein the second polyolefin is selected from the group consisting of polyethylene, polypropylene, and ethylene vinyl acetate.

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19. A polyolefin resin for use in preparing an open cell polyolefin foam article, comprising:

(a) a functionalized polyolefin comprising functional moieties reactive to ammonia; and

25        (b) a foaming agent wherein a majority of the foaming agent is a chemical foaming agent capable of producing ammonia.

20. The composition of claim 19, wherein the foaming agent comprises a chemical foaming agent and a physical foaming agent, the physical foaming agent present in an amount of less than 15 wt% total foaming agent.

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21. The polyolefin resin of claim 19, wherein the chemical blowing agent is selected from the group consisting of azodicarbonamide, p-toluenesulfonyl semicarbazide, 5-phenyltetrazole or combinations thereof.

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22. The polyolefin resin of claim 19, wherein the polymer composition further comprises a crosslinking agent.

23. The polyolefin resin of claim 19, wherein the crosslinking agent is a peroxide.

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24. The polyolefin resin of claim 19, wherein the functional moiety is selected from the group consisting of carbonyl, epoxides, anhydrides and organic acid groups.

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25. The polyolefin resin of claim 19, wherein the ammonia-reactive functional moiety comprises at least 3 wt% of the functionalized polyolefin.

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26. The polyolefin resin of claim 19, wherein the ammonia-reactive functional moiety comprises at least 5 wt% of the functionalized polyolefin.

27. The polyolefin resin of claim 19, wherein the ammonia-reactive functional moiety comprises 1-20 wt% of the functionalized polyolefin.

5        28. The polyolefin resin of claim 19, wherein the polymer composition has a melt index in the range of 0.3 to 10.

29. The polyolefin resin of claim 19, wherein the polymer composition further comprises a surfactant.

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30. An open cell polyolefin foam article, comprising:  
a crosslinked polyolefin having an open cell ratio of greater than 60% and a gel fraction of greater than 50%, wherein the crosslink comprises a nitrogen atom.

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31. A method for a producing an open-celled, cross linked polycarbonate foam article, comprising:

(a) providing a polymer composition comprising:

20        (i) a polycarbonate having a functional moiety reactive to ammonia, and

      (ii) a foaming agent wherein the foaming agent is a chemical foaming agent capable of producing ammonia; and

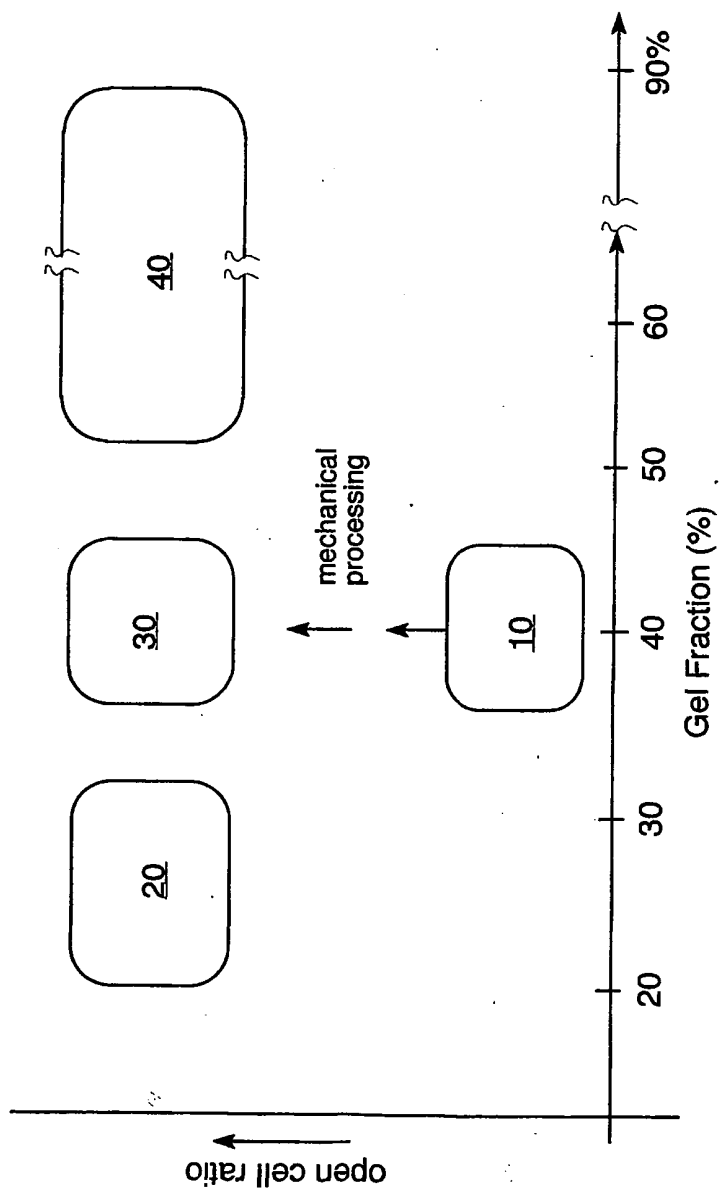
25        (b) activating the chemical foaming agent to generate a gaseous blowing agent and ammonia, whereby the blowing agent forms an open cell foam article and the ammonia chemically crosslinks the polycarbonate at the ammonia-reactive sites.

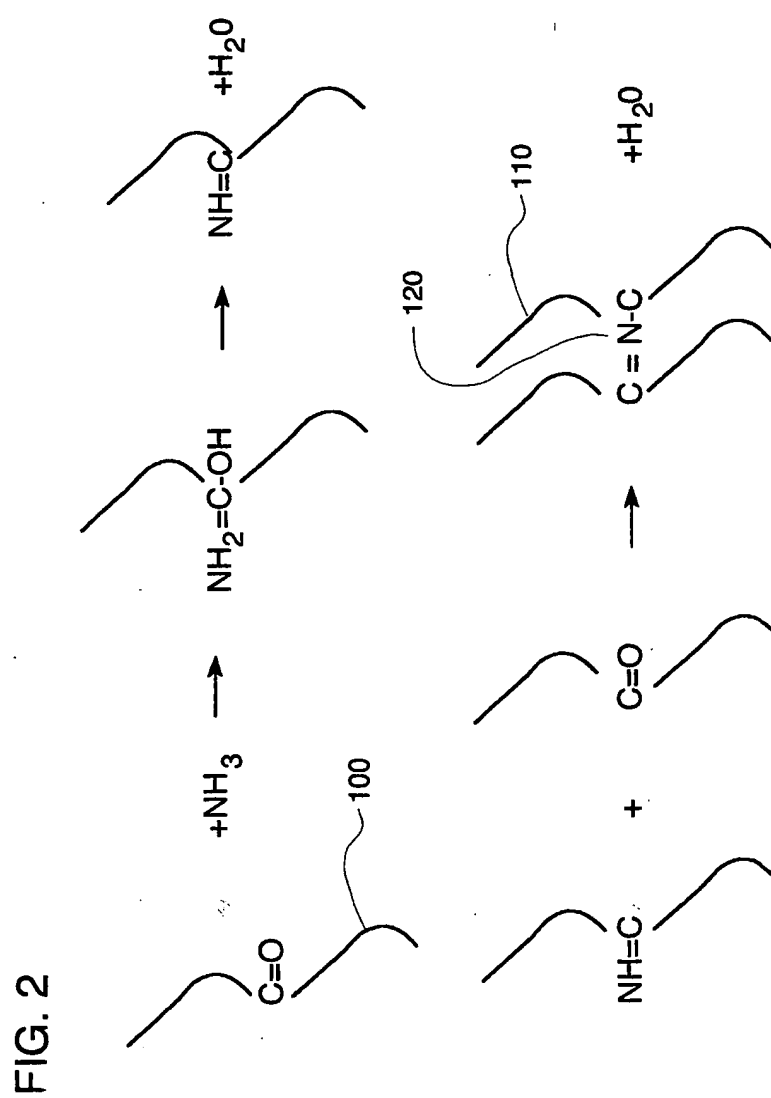


32. The method of claim 31, wherein the polycarbonate comprises bisphenol.

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FIG. 1





## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/25776

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B29C 44/09; C08J 9/06, 9/10, 9/12

US CL : 264/54; 521/94, 134, 182

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 264/54; 521/94, 134, 182

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,780,140 A (HAMMER) 18 December 1973.	1-30
Y	US 4,532,307 A (TADA) 30 July 1985, see the entire document.	1-30
A	US 5,356,941 A (SULLIVAN et al.) 18 October 1994.	1-30

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

Special categories of cited documents:	
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*O* document referring to an oral disclosure, use, exhibition or other means	*G* document member of the same patent family
*P* document published prior to the international filing date but later than the priority date claimed	

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